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STUDY OF CRACK INITIATION PHENOMENA ASSOCIATED WITH STRESS CORROSION OF ALUMINUM ALLOYS

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LITERATURE SURVEY

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INTRODUCTION

There is an increasing literature dealing with the initiation of stress-corrosion cracks, but much of it covers the overall stress-corrosion process and does not distinguish between the stages of initiation and propagation. Consequently, much of the present survey is devoted to the whole process rather than to the initiation stage alone. This should be of little concern, however, because most of the conditions which pertain to crack propagation within a material are generally present on the surface and are important to crack initiation.

Several surveys of the literature dealing with the mechanism of stress-corrosion cracking have been made in the last few years (1-5). In each case, it is apparent that the reviewer was faced with a number of serious problems: the sheer volume of literature, the disagreement among different investigators, and looseness in the criteria used for establishing stress-corrosion susceptibility and for reporting experimental conditions. Another problem is largely one of semantics; some workers consider that phenomena such as hydrogen embrittlement, liquid metal embrittlement, and even the cracking of non-metallic materials should all be regarded as stress-corrosion cracking.

POSSIBLE MECHANISMS OF STRESS-CORROSION CRACKING

Merely to specify the conditions that are necessary and sufficient for stress-corrosion cracking does not explain how the process occurs, and a major divergence of opinion exists in this area. Many of the mechanisms that have been proposed fall into two groups; those in which cracking involves mechanical failure steps and those in which the crack proceeds along a path where electrochemical dissolution has occurred.

Observed rates of stress-corrosion cracking are generally very much slower than those of mechanical cracking, but very much faster than penetration rates normally encountered in corrosion phenomena. This fact led Keating (6) to propose an electrochemical-mechanical mechanism of stress-corrosion cracking in which alternate steps of corrosion and brittle cracking occur. Keating recognized that the main difficulty with this mechanism is in explaining how a brittle crack can occur in an otherwise ductile metal (2), for it is generally believed that stress-corrosion cracking occurs only in alloys that exhibit macroscopic ductility.

Experimental evidence in favor of the electrochemical-mechanical mechanism is basically of two types. The first type is evidence of sudden, short steps during a stress-corrosion test while the second type is evidence obtained by examination of fractured surfaces after stress corrosion has occurred.

Evidence of the first type includes acoustical indications, solution potential indications, and extensometer indications.

Van Rooyen (7) has pointed out some of the pitfalls of the acoustical method; for example, bursting hydrogen bubbles might produce sounds that could be confused with brittle fracture steps. Parkins (8) has pointed out the shortcomings of the solution potential method, in particular, the fact that the change in conditions at the crack tip would seem to be too localized to have any effect on the macroscopic solution potential. Extensometer indications are probably the most suspect of all. In mild steels, a jerky type of yielding is obtained even in a tensile test because of strain aging (8). In at least one instance, discontinuous steps in extensometer readings were produced by the testing equipment itself (2).

The strongest evidence in favor of electrochemicalmechanical steps in the stress-corrosion process is electron
microscopic observations of striations in the fractured surface (9-10). The striations, however, cannot be taken as
unequivocal evidence of mechanical failure steps since it
is conceivable that they could also reflect steps of plastic
flow on alternating crystallographic planes. In any case,
striations have not been observed on fractured surfaces of
aluminum alloys. The only evidence for the electrochemicalmechanical mechanism in aluminum alloys has been that obtained

by indirect methods (acoustical, solution potential or extension extension) during actual stress-corrosion tests.

Evidence for an electrochemical dissolution feature of the stress-corrosion cracking process seems irrefutable. The process can be both slowed down by cathodic polarization (11) and accelerated by anodic polarization (12). The simplest mechanism of stress-corrosion cracking is one whereby the crack consists of a path where nothing but electrochemical dissolution has occurred. A major objection usually raised to this mechanism is that corrosion rates would have to be prohibitively high in order to account for observed rates of crack propagation. Work by several authors including Nielsen (13) and Edeleanu (14) demonstrates that high corrosion rates can in fact occur along very localized paths. This so-called "tunneling" corrosion has been proposed as the basis of a stress-corrosion cracking mechanism by Swann and Embury (15).

Hoar and West suggest that a high anodic dissolution rate is possible as a result of depolarization brought about by the yielding of metal at the tip of a crack (16). Their mechanism explains not only the role of electrochemical dissolution but also the fact that microscopic yielding has been observed during stress-corrosion cracking.

Experimental verification of Hoar's and West's mechanism has been attempted by several workers, but with conflicting results (2, 17). A variation of Hoar's and West's mechanism

was proposed by Logan in which the depolarization was associated with localized fracture of a brittle oxide film on the surface of the yielding metal (18). Hoar now concedes that this mechanism may well apply to some systems (19).

Several mechanisms that have been proposed would seem to be of limited value in explaining stress-corrosion cracking phenomena. Such mechanisms include wedging of a crack by solid corrosion product (20), brittle failure of a new phase formed by yielding (21), dissolution of an anodic phase formed by reaction with hydrogen (22), various forms of hydrogen embrittlement (23-25), and cyclic cracking and re-formation of a brittle surface film (26).

A simple model of electrochemical dissolution does not explain adequately the specific nature of an environment that is so characteristic in producing stress-corrosion cracking. Such a model would predict similar stress-corrosion behavior in related electrolytes of comparable ionic strengths. It would not predict the selectivity of the chloride, hydroxide and nitrate ions, for example. To account for the specific nature of such ions, Uhlig has suggested that interfacial cracking or stress-sorption cracking as a mode of failure acts conjointly with electrochemical action to cause stress-corrosion cracking of many metals (27).

FACTORS AFFECTING STRESS CORROSION CRACKING

Considering the factors responsible for stress-corrosion cracking, T. P. Hoar has stated, "To get cracking, we require

particular properties of the metal lattice, of the solution, and particular conditions of the interface between them." It is convenient to consider the conditions affecting cracking under the three headings suggested by Hoar.

A. Factors Related to the Metal

Composition - Until recently, it was considered that pure metals were not susceptible to stress-corrosion cracking.

Recent work has shown that stress-corrosion cracking can apparently occur in whiskers of pure iron (28), in pure aluminum (3), in pure copper (29), and in commercial purity titanium (30). Barnartt (31), however, suggests that stress-corrosion cracking should be considered a criterion of purity and that any metal that fails by stress-corrosion cracking must be assumed to be impure. Long and Uhlig support this view with their work indicating that carbon contents as low as a few parts per million can produce stress-corrosion cracking in appropriately heat treated alpha iron (32). Thompson and Tracy have shown that a phosphorous content in copper as low as 0.004% can render it susceptible to stress-corrosion cracking in an ammonia atmosphere (33).

Not all minor alloying elements have detrimental effects on stress-corrosion resistance. Benefits in the stresscorrosion resistance of aluminum alloys have been attributed to the addition of small amounts of iron, silicon, chromium, manganese, zirconium, titanium and silver. These elements each have several effects on the microstructure (34-40) of aluminum alloys and it is not always clear which of them is important to the stress-corrosion process.

The effects of major alloying elements on stress-corrosion cracking have been studied in some detail for many alloy systems. Graf (41) has attempted to relate stress-corrosion performance to the electrochemical nobilities of the components in an alloy. Many authors have studied the effects of the major alloying elements in austenitic stainless steels and in particular the beneficial effect of nickel (27, 42). Considerable interest has been devoted to the copper-zinc system, since the mode of cracking can be altered from intergranular to transgranular by altering the zinc content of the alloy (15). Gruhl has studied the effects of magnesium and zinc on the stresscorrosion cracking of aluminum alloys (40). He concludes that susceptibility to stress-corrosion cracking increases with the sum of the zinc and magnesium contents, but that magnesium has a more deleterious effect than zinc, so that a high zinc-tomagnesium ratio is beneficial.

Explanations for the effects of alloying elements on stress-corrosion behavior are generally associated with their effects on metallurgical structure and are covered in more detail in the next section.

<u>Metallurgical Structure</u> - For most alloys, susceptibility to stress-corrosion cracking can be correlated with certain structural features. Transgranular stress-corrosion cracking

of stainless steel has been correlated with the presence of planar arrays of dislocations (43). Factors which can lead to these arrays are low stacking fault energy or a degree of short-range The beneficial effect of nickel on the stress-corrosion resistance of stainless steel has been attributed to the fact that it raises the stacking fault energy and, hence, reduces the tendency to form planar dislocation arrays (15). Short-range order is capable of causing planar arrays of dislocation even in alloys with high stacking fault energy since slip on an existing plane where the order has already been destroyed is easier than slip on a new plane. The important dislocations in aluminum alloys are generally accepted to be those confined to the regions adjacent to grain boundaries. Recent work by Jacobs (44) on 7075 aluminum alloy suggests that susceptibility in 7075 aluminum alloy can be correlated with the presence of dislocation networks, but his work has not been confirmed.

Metallurgical structure in aluminum alloys is very strongly influenced by thermal treatment. A degree of inhomogeneity is required in an aluminum alloy for susceptibility to stress-corrosion cracking. This inhomogeneity can be brought about in several ways. The most common way is the standard solution heat treatment, quench and aging sequence used to produce high strength structures. The method of quenching is found in many cases to have a pronounced effect on stress-corrosion susceptibility, but the

effect differs for different aluminum alloys; a slow quench can be beneficial for aluminum-zinc-magnesium alloys but detrimental for other alloys (24).

A great deal of attention has been devoted to the effects of aging on the susceptibility to stress-corrosion cracking in aluminum alloys. As pointed out earlier, it is now generally agreed that maximum susceptibility occurs at about the same time as the first sign of grain boundary precipitate. Thomas and Nutting (38) have suggested that the importance of grain boundary precipitate is to restrict dislocation movement to a narrow band on either side of the grain boundary.

Mears, Brown and Dix considered the regions adjacent to grain boundaries to be depleted in solute as a result of the precipitation at the boundaries (11). Perryman has drawn attention to the so-called "light phenomenon" observed by Gayler (45) and Perryman and Blade (46) which appeared to be associated with maximum susceptibility in binary aluminum alloys. The phenomenon is observed in the light microscope as a zone adjacent to a grain boundary that "lights up" when the focus is altered slightly. Perryman suggests that the zone is a recrystallized region of solid solution in equilibrium at the aging temperature. A more recent explanation (38) is that the precipitate-free zone adjacent to a grain boundary represents a region from which most of the vacancies have diffused to the boundaries. The lack of vacancies would then retard precipitation. On this premise, Thomas has

devised a treatment in which aging is interrupted, cold work is applied to introduce vacancies, and then the aging is continued (47). Clark presents evidence that the precipitate-free zone adjacent to grain boundaries in an aluminum-silver alloy is not depleted of solute; the lack of precipitate again is attributed to the depletion of vacancies (48).

One effect of heat treatment that might be overlooked is that the composition of surface layers may be altered. For example, an aluminum-magnesium alloy will lose magnesium from the surface during heat treatment and this effect has in fact been reported to improve its stress-corrosion resistance (49).

Gruhl has shown that deformation of an aluminum-zinc-magnesium alloy improves its resistance to stress-corrosion cracking. Interestingly, the improvement became less as the applied stress increased and was lost as the applied stress approached the yield strength (50).

Grain structure has a pronounced effect upon the stress-corrosion susceptibility of aluminum alloys. Sprowls and Brown (51) describe the considerable variation in susceptibility that can be encountered in one product by simply taking specimens with different orientations with respect to the grain structure. A general rule is that resistance to stress-corrosion cracking is a maximum in the long direction of the grains.

B. Environmental Factors

There is a substantial literature dealing with the effect of environment on stress-corrosion cracking. Romanov has surveyed the literature dealing with the effect of environment on alloys generally (52) and Rolles and Vandenburgh have surveyed the literature dealing specifically with the effects of environment on aluminum alloys (53). The Corrosion Committee of the American Society for Testing Materials has also prepared surveys for various metals but these may not be readily available.

Over the years, environments that promote stress-corrosion cracking best in various alloys have become very well recognized. To list just a few examples, chlorides are effective for aluminum alloys, ammonia for brass, hydroxide and nitrates for low-carbon steels, chlorides and hydroxides for austenitic stainless steels, and mixtures of chlorides and chromates for magnesium alloys (4).

Much of the work on aluminum alloys has been directed toward establishing and controlling conditions in accelerated stress-corrosion tests. A surprising number of environmental conditions affect stress-corrosion performance. For example, in accelerated tests in a sodium chloride solution, performance is affected by the water used to prepare the solution (54); and when these tests are carried out by alternate immersion, performance is affected by atmospheric conditions (49). Even moisture has produced stress-corrosion cracking in aluminum

alloys (49, 55), although it cannot be assumed that the moisture was not mildly corrosive because of the possibility of contamination. Stress-corrosion cracking of some of the more highly susceptible aluminum alloys in the atmosphere itself is not uncommon (56).

Most accelerated stress-corrosion tests for aluminum alloys are based upon exposure in a sodium chloride solution. One reason is that the sea and marine atmosphere are important service exposures, but its use depends primarily upon the fact that chlorides are particularly effective in producing stress-corrosion cracking in aluminum alloys. The concentration of a sodium chloride solution is important as demonstrated by Perryman and Hadden who found that the rate of stress-corrosion cracking of a susceptible aluminum - 7% magnesium alloy in a sodium chloride solution increased up to a salt concentration of 9% by weight (49). They also demonstrated that oxygen accelerated stress-corrosion cracking, most likely because its reduction is one of the most feasible cathodic reactions.

Gilbert and Hadden (57) and Vosskuhler (58) (among others) have pointed out that stress-corrosion cracking of aluminum alloys in a sodium chloride solution is accelerated by acidification of the solution. Acidified sodium chloride solutions have been used by Sprowls and Lifka (56), and Gilbert and Hadden (57), as well as by others, for accelerated corrosion tests for aluminum alloys. English has demonstrated

the effectiveness of a sodium chloride solution acidified with hydrochloric acid and buffered with aluminum chloride (59). In a sodium chloride solution, anodic dissolution of aluminum leads to an acidic condition; as a result, acceleration of stress-corrosion cracking would be expected by the addition of acid or buffers that promote or maintain this condition.

Gruhl (50) and others have presented data showing that stress-corrosion cracking of aluminum alloys in a sodium chloride solution is accelerated by raising the temperature of the solution. Recently, Helfrich presented data for an aluminum-zinc-magnesium alloy indicating an Arrhenius type dependence of stress-corrosion rate upon temperature; he used these data as evidence that stress-corrosion cracking is an activated process (60).

Few generalizations can be made about the effect of environment on stress-corrosion cracking. The most common generalization perhaps is that stress-corrosion cracking requires only a mildly corrosive environment, or alternatively, that to promote stress-corrosion cracking, general corrosion should be minimized.

A simple electrochemical concept suggests that stress-corrosion cracking depends not upon metallurgical structure alone, nor upon the electrochemical characteristics of this structure alone, but rather upon these two factors acting together, in a specific environment. To illustrate, Mears,

Brown and Dix attributed the stress-corrosion performance of an aluminum - 10% magnesium alloy in two electrolytes to the electrochemical relationships between the grain boundary precipitate and the solid solution matrix (11). In the electrolyte in which the precipitate was anodic to the matrix, the alloy was susceptible to stress-corrosion cracking, while in the electrolyte in which the precipitate was cathodic to the matrix, it was not susceptible.

The stress-sorption theory proposed by Uhlig (27) is based upon the specificity of an environment, or upon the presence of a "critical species" to use the term of Pugh and Westwood (29). The "critical species," however, cannot be predicted. Presumably, the species adsorbed depends upon surface and interfacial energy relationships but there is little experimental data from which these relationships can be derived.

Recent work by Overman indicates that inhibition of stress-corrosion cracking of stainless steel by certain anions is a result of competition for adsorption sites on the metal surface (61). An addition of sufficient phosphate ions to a chloride solution prevents stress-corrosion cracking; Overman attributed this result to displacement of adsorbed chloride ions by phosphate ions.

C. Factors Related to the Metal-Environment Interface

In considering the initiation of stress-corrosion cracking, the metal-environment interface is of paramount importance because it is here that the structure of the alloy is acted upon by the environment. At this interface, certain features of the stress-corrosion process are simplified because there has been insufficient reaction to alter locally the composition of the environment. Also, crevices and cracks have not formed to complicate the process of feeding the environment to the reaction front. The stress-corrosion process is somewhat complicated at this interface, however, by the existence of films which have been formed naturally on the surface of the metal and which must be breached by the environment.

According to a simple electrochemical concept, a stress-corrosion crack should initiate at any site where galvanic relationships lead to selective corrosion. In aluminum-copper alloys, a suitable site for selective corrosion is the region adjacent to a grain boundary, because this region is depleted in copper in solid solution and, therefore, anodic both to precipitate in the boundary and to the precipitate-free grain body itself. In aluminum-magnesium alloys, an anodic site suitable for selective corrosion is the equilibrium precipitate along a grain boundary. With these alloys, maximum susceptibility to stress-corrosion cracking might be expected where grain boundary precipitate is continuous. More recent evidence suggests that maximum susceptibility occurs at the same time as the first sign of grain boundary precipitate (62-64).

In the presentation of their generalized theory of stresscorrosion cracking, Mears, Brown and Dix (11) called attention to the effect of notches developed on the metal surface by intergranular corrosion. These sharp notches acted as stress raisers, increased the effective stress at the root of the crevice, and thereby accelerated failure by stress corrosion. They also pointed out the relationship between rate of stress-corrosion cracking and the number of corrosion sites or notches, where a large number of notches reduces the rate of cracking by decreasing the stress intensity at any single notch.

Mears, Brown and Dix did not consider, however, the case of stress-corrosion cracking in aluminum alloys that are not susceptible to intergranular corrosion in the unstressed condition. Also, some aluminum alloys - most notably the aluminum-magnesium-silicide alloys - are susceptible to intergranular corrosion but not to stress-corrosion cracking. A good example, which also emphasizes the importance of environment, is given by Perryman and Blade (65). They describe an experiment in which an aluminum-magnesium alloy heat treated to be very susceptible to stress-corrosion cracking in chloride solutions was immersed in 5% phosphoric acid. The alloy disintegrated into grains in a manner that was unaffected by stress.

Recently, McHardy (66) investigated the development of intergranular stress-corrosion cracking in 7075 aluminum alloy in the aggressive electrolyte used earlier by English (59); in the unstressed condition the alloy was subject only to pitting attack. McHardy presented electron microscopic evidence that

the first sign of intergranular attack in the stressed condition was associated with pits. It would appear that the initiation of intergranular attack in this case requires a high stress and that the role of pitting is to act as a stress raiser.

Brown and Beachem contend that most high-strength steels, although susceptible to stress-corrosion cracking in aqueous environments, require a stress raiser to initiate the process (67). For stress-corrosion testing, they propose a notched specimen stressed as a cantilever beam in which the notch is "sharpened" by the development of a fatigue crack. The stress at the root of the crack is calculated from equations derived from fracture mechanics. The lives of stressed specimens are related to stress intensities at the base of the notches in the same way they are related conventionally to the applied stresses.

Mulherin has applied the method of Brown and Beachem to strong aluminum alloys (68). He found a substantial difference between alloys that differed only slightly in resistance to stress-corrosion cracking as evaluated by conventional methods. He noted that the different results obtained with the method of Brown and Beachem and with conventional methods raised "A question on the relative importance of the crack initiation period as compared to the crack propagation phase;" he did not attempt to answer the question.

Gruhl demonstrated an effect of pre-corrosion on the resistance to stress-corrosion cracking of an aluminum-zinc-magnesium alloy (69). Specimens were pre-corroded unstressed and then stressed without being removed from the corrosive solution. The life of a stressed specimen first decreased linearly with the period of pre-corrosion and then leveled

off without further change. Gruhl concludes that the stage when the life decreases with pre-corrosion is a "preparatory period" in which a chemical or electrochemical reaction equilibrium occurs between the corrosion agent and the metal surface of the grain boundaries. During this period, protective oxide or coating layers must be loosened and penetrated by the corrosion agent, so that the reaction necessary for the stress-corrosion cracking can occur.

Hoar points out that corrosion pits need to be deep and narrow fissures before stress-corrosion cracking can occur (2). He reports that austenitic stainless steels exposed to chloride solutions develop flat bottomed or shallow pits which, not being fissured, cannot appreciably raise stress. Hoar proposes that certain narrow regions of "disarrayed metal" can dissolve preferentially, and in depth, to produce narrow, probably submicroscopic fissures that develop a substantial increase in local stress at their bases and so start the propagation mechanism. Regions of "disarray" might be grain boundaries, subgrain boundaries, emergent dislocations, or strained regions produced by local quenching stresses or cold work. Hoar terms his mechanism a "mechanochemical effect" and defines it briefly as anodic dissolution greatly assisted by simultaneous yielding.

Neilsen demonstrated that "corrosion tunnels" can develop by anodic action within minutes on a stressed surface of an 18-8 stainless steel exposed to hot aqueous 42% MgCl₂ (13). Utilizing oxide extraction replicas and electron stereomicroscopy techniques, the paths of initial corrosive attack were found to be tunnels of submicroscopic cross section. The chloride ion is believed to diffuse preferentially down "pipes" of extended dislocations or stacking faults in the lattice. Prolonged exposure allows lateral corrosion and merging of adjacent tunnels to produce microcrevices.

Swann and Nutting also suggest that preferential dissolution of stacking faults might provide the kind of narrow fissure required to initiate cracks (70).

Barnartt, Stickler and Van Rooyen point out that their "cracking" steels had low stacking fault energies and their "immune" steels had high stacking fault energies (71).

Hoar comments that if either stacking faults or emergent pile-ups can initiate cracks, and if restricted slip can propagate them, then a coherent theory for the mechanism of stress-corrosion cracking of austenitic steels is being approached, and this type of trouble may be avoided by using lattices with high stacking fault energy and easy cross slip (2).

Tromans and Nutting, using electron microscopy, attempt to consolidate the work of various investigators on crack initiation in face centered cubic metals (72). They conclude that the principal sites of crack initiation in both intergranular and transgranular modes of failure are dislocations. Preferential dissolution of dislocations in continuous regions of high dislocation density produces a series of microcracks

(pits) which link to form macrocracks. The continuous regions are grain boundaries for intergranular failure, and octahedral planes containing planar arrays of dislocations for transgranular failure. The requirement for planar arrays in transgranular stress-corrosion cracking is explained by considering the manner in which cracks begin. Selective dissolution of material at surface emergent ends of dislocations produces a series of small pits, which link to form microcracks. These subsequently link to form macrocracks. Therefore, ease of crack formation should be related directly to pit distribution. Linear arrays of closely spaced pits is considered the ideal distribution. Pits are able to link easily and linkage produces a thin slit capable of propagating under applied stress. In order to achieve ideal distribution, dislocations initiating the pits must be closely spaced and arranged in linear arrays. This is another way of stating that the alloy must contain a planar arrangement of dislocations. This mechanism implies crack initiation along the slip planes on which the arrays lie. Analyses showed crack formation along octahedral planes, providing experimental support for the mechanism.

Tromans and Nutting also point out that, while many features of stress-corrosion cracking may be explained in terms of dislocation dissolution, another apparently basic requirement for initiation is solute segregation. Accepting that solute segregation is necessary for production of stress-corrosion cracking sites, they are able to account for differences

in stress-corrosion cracking performance which cannot be explained solely in terms of dislocation dissolution.

Brief mention should be made of the mechanism proposed by Forty and Humble (73). These authors propose that stress-corrosion cracking, at least in the particular system they studied (brass - ammonia), occurs not in the metal but in the surface film itself. The crack is propagated by repeated formation and rupture of a tarnish film. Tromans and Nutting (72) studying the same system concluded that the cracks that formed in the tarnish film were not sufficient to account for stress-corrosion cracking.

Gulbransen and Copan (74) suggest that sites for initiation of oxide platelets in air can be governed by an applied stress. According to them, the function of an applied stress is to generate active sites in the surface, presumably by a process of slow creep.

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There is a rather extensive literature dealing with stress-corrosion cracking. Relatively little of it is concerned directly with crack initiation but much of it is relevant to this topic.

An electrochemical aspect of the initiation and propagation of stress-corrosion cracks in aluminum alloys is well established.

Certain of the metallurgical features that control electrochemical relationships in these alloys are equally well established. There

is evidence of the importance of notches, developed during the initial stages of corrosion acting as stress raisers and, in combination with the applied stress, changing the existing. electrochemical relationships. There is also evidence that surface films and surface-sorbed ions are important to the stress-corrosion mechanism. All of this varied evidence, however, does not give a complete understanding of the stress corrosion of aluminum alloys, and many doubts remain, particularly concerning the inception of the stress-corrosion process. There is a need to know the behavior of the various minute microstructural features at the start of a corrosion exposure, the effect of such features once corrosion has started and selective paths develop, the function of both artificial and self-generated surface irregularities, the interplay of applied stress and topographical stress raisers, and the function of films in controlling and directing the stress-corrosion process.

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BIBLIOGRAPHY

- 1. R. N. Parkins, "Stress-Corrosion Cracking," Metallurgical Reviews, 9, No. 35 (1964).
- 2. T. P. Hoar, "Stress-Corrosion Cracking," p. 14, Second International Congress on Metallic Corrosion (1963), National Association of Corrosion Engineers, Houston, Texas.
- 3. E. N. Pugh, "On the Mechanism(s) of Stress-Corrosion Cracking," First Technical Report, Army Research Office (Durham) Project, DA-31-124-ARO-D-258, (August, 1965), Research Institute for Advanced Studies, Baltimore, Maryland.
- 4. H. L. Logan, "The Stress-Corrosion Cracking of Metals," p. 33, Metals Engineering Quarterly, American Society for Metals (May, 1965).
- 5. F. H. Haynie, D. A. Vaughan, P. D. Frost and W. K. Boyd, "A Fundamental Investigation of the Nature of Stress-Corrosion Cracking in Aluminum Alloys," Battelle Memorial Institute, Technical Report AFML-TR-65-258 (October, 1965), Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.
- 6. F. H. Keating, "Chemical Manifestations of Internal Stress," p. 311, Symposium on Internal Stresses in Metals and Alloys, (Book) (1948) Institute of Metals Monograph and Report Series No. 5, London.
- 7. D. Van Rooyen, "Qualitative Mechanism of Stress-Corrosion Cracking of Austenitic Stainless Steels," Corrosion, 16, 421t, (1960).
- 8. R. N. Parkins, Lecture, "Some Aspects of the Influence of Deformation and Structure on Stress-Corrosion Cracking of Mild Steels," U. S. Steel Research Center (March 30, 1966).
- 9. L. Fairman and J. M. West, "Stress-Corrosion Cracking of a Magnesium Aluminum Alloy," Corrosion Science, 5, No. 10, 711 (1965).
- 10. H. L. Logan, M. J. McBee, and D. J. Kahan, "Evidence for an Electrochemical-Mechanical Stress-Corrosion Fracture in a Stainless Steel," Corrosion Science, 5, No. 10, 729 (1965).
- 11. R. B. Mears, R. H. Brown and E. H. Dix, Jr., "A Generalized Theory of the Stress-Corrosion of Alloys," ASTM and AIME Symposium on Stress-Corrosion Cracking of Metals (Book), 323, (1945).
- 12. F. F. Booth and H. P. Godard, "An Anodic Stress-Corrosion Test for Aluminum-Magnesium Alloys," p. 703, First International Congress on Metallic Corrosion (1961), Butterworths, London.

- 13. N. A. Nielsen, "Nature of Initial Corrosion of Stressed Austenitic Stainless Steel by Chloride Ions II Platinum Decoration of Active Sites," p. 116, Second International Congress on Metallic Corrosion (1963), National Association of Corrosion Engineers, Houston, Texas.
- 14. C. Edeleanu, "The Propagation of Corrosion Pits in Metals,"
 The Journal of the Institute of Metals, 89, p. 90 (1960-1961).
- 15. P. R. Swann and J. D. Embury, Second Berkley International Materials Conference on High-Strength Materials, p. 327, (1964), John Wiley.
- 16. T. P. Hoar and J. M. West, "Mechano-Chemical Anodic Dissolution," Nature, 181, p. 835 (1958).
- 17. D. Van Rooyen, "Some Aspects of Stress-Corrosion Cracking in Austenitic Stainless Steels," p. 309, First International Congress on Metallic Corrosion, (1961), Butterworths, London.
- 18. H. L. Logan, "Film-Rupture Mechanism of Stress Corrosion,"
 Journal of Research of the National Bureau of Standards, 48,
 No. 2, (1952).
- 19. T. P. Hoar, Lecture, "Passivity and Stress-Corrosion Cracking," U. S. Steel Research Center, (April 7, 1966).
- 20. N. A. Nielsen, "The Role of Corrosion Products in Crack Propagation in Austenitic Stainless Steel Electron Microscope Studies," p. 121, Physical Metallurgy of Stress-Corrosion Fracture, (Book), (1959), Interscience Publishers, New York.
- 21. J. F. Bates and W. W. Loginow, "Principles of Stress-Corrosion Cracking as Related to Steels," Corrosion, 20, No. 6, p. 189t, (1964).
- 22. D. A. Vaughn, D. I. Phalen, C. L. Peterson and W. K. Boyd, "Relationship Between Hydrogen Pickup and Susceptible Paths in Stress-Corrosion Cracking of Type 304 Stainless Steel," p. 216, Second International Congress on Metallic Corrosion (1963), National Association of Corrosion Engineers, Houston, Texas.
- 23. R. A. Davis, "Stress-Corrosion Cracking Investigation of Two Low Alloy, High-Strength Steels," Corrosion, 19, p. 45t, (1963).
- 24. F. H. Haynie, "The Effect of Theory on the Choice of Test Methods for Determining the Stress-Corrosion Cracking Susceptibility of Aluminum Alloys," ASTM Sixty-Ninth Annual Meeting of the American Society for Testing and Materials, Atlantic City, New Jersey, (June 27 July 1, 1966).

- 25. D. A. Vaughn and D. I. Phalen, "Reactions Contributing to the Formation of Susceptible Paths for Stress-Corrosion Cracking," ASTM Sixty-Ninth Annual Meeting of the American Society for Testing and Materials, Atlantic City, New Jersey, (June 27 July 1, 1966).
- 26. A. J. McEvily and A. P. Bond, "On the Initiation and Growth of Stress-Corrosion Cracks in Tarnished Brass," Journal of the Electrochemical Society, 112, p. 131, (1965).
- 27. H. Uhlig, "New Perspectives in the Stress-Corrosion Problem," p. 1, Physical Metallurgy of Stress-Corrosion Fracture, (Book), (1959), Interscience Publishers, New York.
- 28. J. Flis, J. Mieluch and M. Smialowski, "Electrochemical Behavior and Corrosion of Iron Crystals in Ammonium Nitrate Solutions," Corrosion, 20, p. 184, (1964).
- 29. E. N. Pugh and A. R. C. Westwood, "Critical Species in Stress-Corrosion Phenomena," ASTM Sixty-Ninth Annual Meeting of the American Society for Testing and Materials, Atlantic City, New Jersey, (June 27 July 1, 1966),
- 30. K. Mori, A. Takamura and T. Shimose, "Stress-Corrosion Cracking of Ti and Zr in HCl Methanol Solutions," Corrosion, 22, No. 2, p. 29, (1966).
- 31. S. Barnartt, "General Concepts of Stress-Corrosion Cracking," Corrosion, 18, p. 322, (1962).
- 32. L. M. Long and H. H. Uhlig, "Effect of Carbon and Oxygen in Iron on Stress-Corrosion Cracking in Nitrate Solution," Journal of the Electrochemical Society, 112, p. 964, (1965).
- 33. D. H. Thompson and A. W. Tracy, "Influence of Composition on the Stress-Corrosion Cracking of Some Copper-Base Alloys," AIME, Institute of Metals Division, 185, p. 100, (1949).
- 74. V. Livanov, V. Elagin, E. Ekhina, V. Shteninger and L. Korjakovskaya, "Investigation of Corrosion Under Stress of Al-Zn-Mg Alloys Depending on Additions of Mn, Ti, Zr," Tr. Mosk. Aviats, Tekhnol. Inst., No. 55, p. 49, (1962), Chemical Abstracts, 59, No. 6, 6101 (September 16, 1963).
- 35. R. Chadwick, N. Muir and H. Grainger, "Stress-Corrosion of Wrought Ternary and Complex Alloys of the Aluminum-Zinc-Magnesium System," The Journal of the Institute of Metals, 85, p. 161 (1956-1957).
- 36. R. Elkington, "The Effect of Substructure on the Stress Corrosion of Commercial Al-Zn-Mg Alloys," The Journal of the Institute of Metals, 90, p. 267, (1961-1962).

- 37. E. Liddiard and W. Bell, "The Influence of Extrusion Direction on the Corrosion and Stress Corrosion of Aluminum-Copper-Magnesium Alloys," The Journal of the Institute of Metals, 82, p. 426, (1953-1954).
- 38. G. Thomas and J. Nutting, "The Aging Characteristics of Aluminum Alloys Klectron Microscope Studies of Alloys Based on the Aluminum-Zinc-Magnesium System," The Journal of the Institute of Metals, 88, p. 81, (1959-1960).
- 39. E. H. Dix, Jr., "Aluminum-Zinc-Magnesium Alloys Their Development and Commercial Production," Transactions of the American Society of Metals, 42, (1950).
- 40. W. Gruhl, "The Stress-Corrosion Behavior of the High-Strength Aluminum Alloys," Metall, 19, No. 3, p. 206, (1965).
- 41. L. Graf, "Stress-Corrosion Cracking in Homogeneous Alloys," p. 48, Stress-Corrosion Cracking and Embrittlement (Book), (1954), John Wiley and Sons, Inc., New York.
- 42. H. Copson, "Effect of Nickel Content on the Resistance to Stress-Corrosion Cracking of Iron-Nickel-Chromium Alloys in Chloride Environments," p. 328, First International Congress on Metallic Corrosion, (1961), Butterworths, London.
- 43. D. Douglass, G. Thomas and W. Roser, "Ordering Stacking Faults and Stress-Corrosion Cracking in Austenitic Alloys," p. 66, Second International Congress on Metallic Corrosion, (1963), National Association of Corrosion Engineers, Houston, Texas.
- 44. A. Jacobs, "The Role of Dislocations in the Stress-Corrosion Cracking of 7075 Aluminum Alloy," Transactions Quarterly, Transactions of American Society for Metals, 58, No. 4, p. 579, (1965).
- 45. E. Perryman, "Metallurgical Aspects of Stress-Corrosion Cracking in Aluminum Alloys," p. 61, Stress-Corrosion Cracking and Embrittlement, (1954), John Wiley and Sons, Inc., New York.
- 46. E. Perryman and J. Blade, "Relationship Between the Aging and Stress-Corrosion Properties of Aluminum-Zinc Alloys," The Journal of the Institute of Metals, 77, p. 263, (1950).
- 47. G. Thomas, "Process for Improving Stress-Corrosion Resistance of Age-Hardenable Alloys," United States Patent Office, Patent No. 3,133,839, (May 19, 1964).

- 48. J. B. Clark, "Electron Probe Test of Two Theories of 'Denuded Zone' Formation in Aged Alloys," ACTA Met., 12, No. 10, p. 1197, (1964).
- 49. E. Perryman and S. Hadden, "Stress Corrosion of Aluminum 7% Magnesium Alloy," The Journal of the Institute of Metals, 77, p. 207, (1950).
- 50. W. Gruhl, "Temperature Dependence on the Stress Corrosion of Al-Zn-Mg₃ Alloy," Z. Metallkunde, <u>53</u>, p. 670, (1962).
- 51. D. O. Sprowls and R. H. Brown, "Resistance of Wrought High-Strength Aluminum Alloys to Stress Corrosion," Alcoa Research Laboratories Technical Paper No. 17, (Aluminum Company of America) (1962).
- 52. V. V. Romanov, "Stress-Corrosion Cracking of Metals," (Book), (1961), Israel Program for Scientific Translations, Jerusalem.
- 53. D. Vandenburgh and R. Rolles, "Investigation of Stress-Corrosion Cracking of High-Strength Aluminum Alloys Literature Survey," George C. Marshall Space Flight Center, Contract No. 8-5340, (1963).
- 54. H. Farmery and U. R. Evans, "The Stress Corrosion of Certain Aluminum Alloys," Journal of the Institute of Metals, 84, p. 413, (1955-1956).
- 55. E. H. Dix, Jr., "Acceleration of the Rate of Corrosion by High Constant Stresses," Transactions of the Institute of Metals Division, A.I.M.E., 137, Technical Publication No. 1204, (1940).
- 56. B. W. Lifka and D. O. Sprowls, "Stress-Corrosion Testing of Aluminum Alloy 7079-T6 in Various Environments," ASTM Sixty-Ninth Annual Meeting of the American Society for Testing and Materials, Atlantic City, New Jersey, (June 27 July 1, 1966).
- 57. P. T. Gilbert and S. E. Hadden, "A Theory of the Mechanism of Stress Corrosion in Al 7% Mg Alloy," The Journal of the Institute of Metals, 77, p. 235, (1950).
- 58. H. Vosskuhler, "Appearance and Interpretation of Stress Corrosion in Malleable Aluminum Alloys," Werkstoffe und Korrosion (German), 1, p. 143, (April, 1950); p. 179, (May, 1950); p. 310, (August, 1950); p. 357, (September, 1950).
- 59. G. C. English, "Investigation of the Mechanism of Stress Corrosion of Aluminum Alloys," Bureau of Naval Weapons Contract NOw 64-0170c, Final Report, (1965).

- 60. W. J. Helfrich, "Influence of Stress and Temperature on Short-Transverse Stress-Corrosion Cracking of an Al 4.2% Zn 2.5% Mg Alloy," ASTM Sixty-Ninth Annual Meeting of the American Society for Testing and Materials, Atlantic City, New Jersey, (June 27 July 1, 1966).
- 61. R. F. Overman, "Using Radioactive Tracers to Study Chloride Stress-Corrosion Cracking of Stainless Steels," Corrosion, 22, No. 2, p. 48, (1966).
- 62. C. Edeleanu, "A Mechanism of Stress Corrosion in Aluminum-Magnesium Alloys," The Journal of the Institute of Metals, 80, p. 187, (1951-1952).
- 63. W. D. Robertson, "Correlation of Mechanical Properties and Corrosion Resistance of 24S Type Aluminum Alloys as Affected by High-Temperature Precipitation," A.I.M.E., Institute of Metals Division, 166, p. 216, (1946).
- 64. W. Gruhl, "Electron Microscopic Studies on Stress-Corrosion Specimens of Al-Zn-Mg₃ Alloy," Aluminum, 38, p. 775, (1962).
- 65. E. C. W. Perryman and J. C. Blade, "Relationship Between the Aging and Stress-Corrosion Properties of Aluminum-Zinc Alloys," The Journal of the Institute of Metals, 77, p. 263, (1950), Discussion, p. 641.
- 66. J. McHardy, "Investigation of the Mechanism of Stress Corrosion of Aluminum Alloys," Bureau of Naval Weapons Contract NOw 65-0327-f, Final Report, (1966).
- 67. B. F. Brown and C. D. Beachem, "A Study of the Stress Factor in Corrosion Cracking by Use of the Pre-Cracked Cantilever Beam Specimen," Corrosion Science, 5, p. 745, (1965).
- 68. J. Mulherin, "The Influence of Environment on the Crack Propagation Characteristics of High-Strength Aluminum Alloys," ASTM Sixty-Ninth Annual Meeting of the American Society for Testing and Materials, Atlantic City, New Jersey, (June 27 July 1, 1966).
- 69. W. Gruhl, "Study of the Problem of the Stress-Corrosion Behavior of Al-Zn-Mg3," Z. Metallk., 54, p. 86, (1963).
- 70. P. R. Swann and J. Nutting, "The Influence of Stacking-Fault Energy on the Modes of Deformation of Polycrystalline Copper Alloys," Journal of the Institute of Metals, 90, p. 133, (1961-1962).
- 71. S. Barnartt, R. Stickler and D. Van Rooyen, Corrosion Science, 3, No. 9, (1963).

- 72. D. Tromans and J. Nutting, "Stress-Corrosion Cracking of Face-Centered-Cubic Alloys," Corrosion, 21, No. 5, p. 143, (1965).
- 73. A. Forty and P. Humble, "Surface Embrittlement and Stress-Corrosion Cracking of Brass in a Tarnishing Solution," p. 80, Second International Congress on Metallic Corrosion, (1963); National Association of Corrosion Engineers, Houston, Texas.
- 74. E. Gulbransen and T. Copan, "Effect of Stress and Environment on the Microtopology of the Corrosion Product," p. 155, Physical Metallurgy of Stress-Corrosion Fracture, (Book), (1959), Interscience Publishers, New York.